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6. AUTHOR(S) Prof Richard D. Chambers				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) University of Durham South Road Durham DH1 3LE United Kingdom			8. PERFORMING ORGANIZATION REPORT NUMBER N/A	
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Report on the synthesis of a lubricant sample (REF SPC 94-4036)
and an extra sample

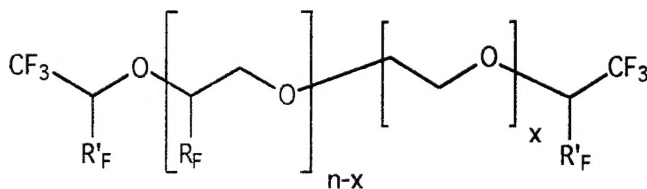
Prof. R.D. Chambers & Dr. M.P. Greenhall, University of Durham, UK.

(This report completes the agreement)

September 20, 1994

Introduction

The objective of this project was to further develop the techniques associated with the preparation of samples of substituted perfluoropolyethers, including the preparation of a 10 to 20 gram sample of perfluoropolyether (1) for lubricant testing by the USAF.



(1)

($n = \text{ca } 45$, $n-x = \text{ca } 26$)
($\text{R}'\text{F} = \text{CF}_3\text{CF}_2\text{CF}_2$, $\text{R}'\text{F} = \text{R}'\text{F}$ (predom) or F, all unmarked bonds to F)

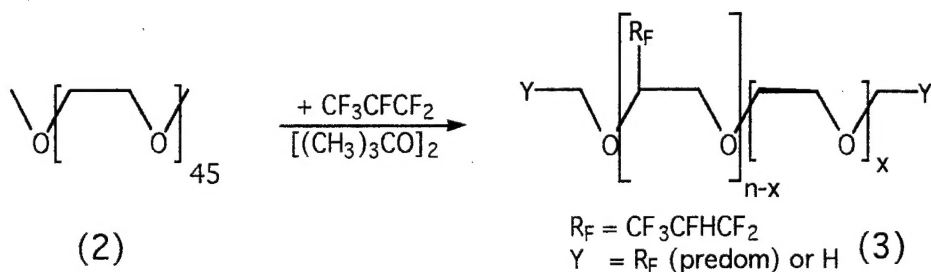
(Note: Chambers, US Patent 4,877,905)

Experimental

a) Starting materials

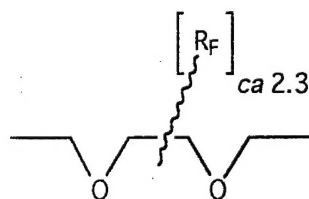
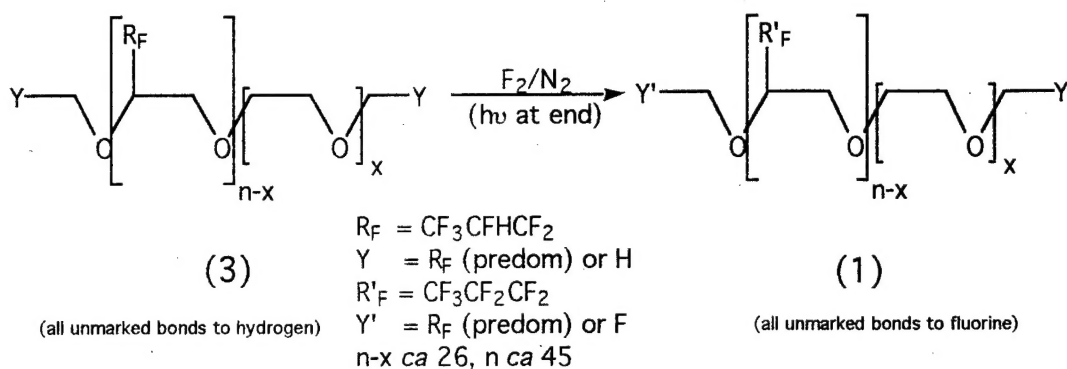
Dimethylpolyethylene glycol(2000) ($n = 45$) was supplied by Merck-Schuchardt, ditertiarybutylperoxide was supplied by Aldrich Chemical Company Limited. Hexafluoropropene was supplied by Fluorochem Limited. 50% Fluorine/Nitrogen mixture was supplied by Air Products.

b) Reaction of Dimethylpolyethylene glycol (2) with hexafluoropropene



Dimethylpolyethyleneglycol(2000) was dried at 140°C under vacuum for a period of 6 hours and was then introduced (457g, 0.225moles), into a one litre stirred autoclave. Ditertiary butyl peroxide (25ml) was also introduced. The stirred autoclave was heated to 80°C and was flushed with nitrogen (three times at a pressure of 20 atmospheres). After evacuation, hexafluoropropene was charged into the autoclave at a pressure of 5 atmospheres. The autoclave was then heated to 140°C and the hexafluoropropene pressure was increased to 20 atmospheres, with stirring. The temperature was maintained between 140-145°C with occasional cooling through water cooling coils for a period of one hour. After cooling, a pale green liquid was withdrawn (882g, after pumping under vacuum for one hour, 857g) which nmr indicated had an average of 13.1 hexafluoroisopropyl groups per molecule. The majority (609g, ca 0.15moles) was reintroduced into the autoclave along with fresh initiator (25ml). After a second reaction an orange oil (869g) was withdrawn. After pumping nmr indicated an average of ca 25.7 hexafluoropropyl units per molecule. A 3rd reaction increased this to about 28 units per molecule.

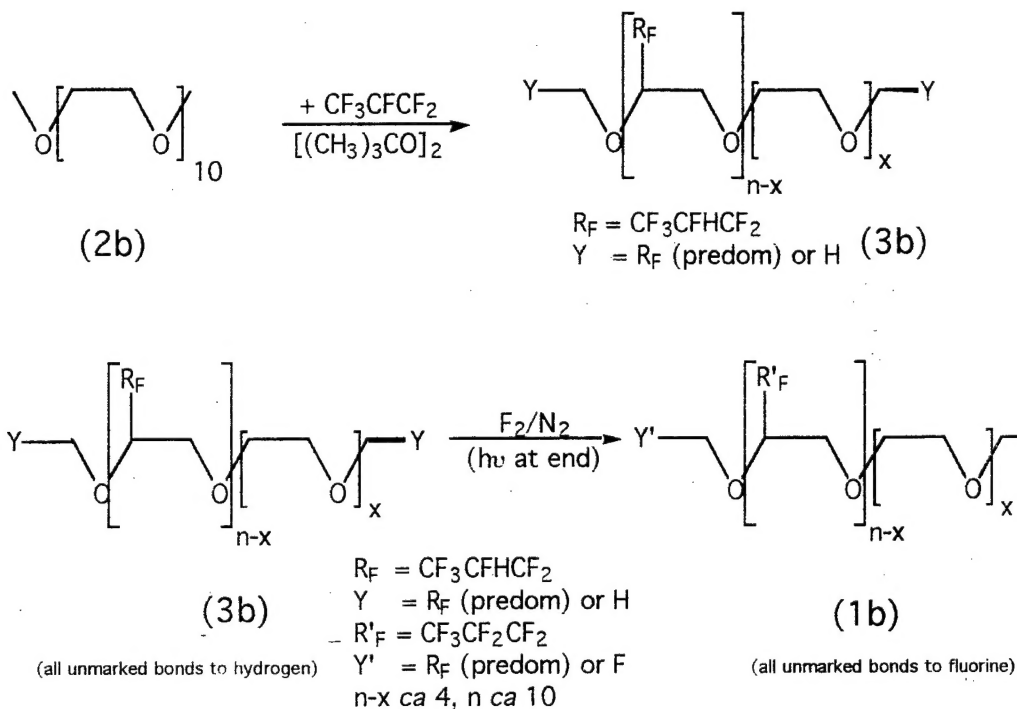
c) Reaction of (3) with fluorine/nitrogen mixtures



(4) (all unmarked bonds to hydrogen)

A solution of (3) (20.7g) in (4) (107.4g) was introduced into a stirred FEP reaction vessel. A F_2/N_2 mixture containing initially 5% F_2 rising to 50% F_2 , was passed into the vessel at room temperature. When the reactivity had decreased the mixture was transferred into an FEP tube through which 50% F_2/N_2 was bubbled. At this time ca 50% of the hydrogen atoms had been replaced by fluorine. Perfluorination was effected by passing 50% F_2/N_2 through the mixture under ultra violet irradiation (100W then 1000W). The volatile, now perfluorinated, solvent (87g) was removed under reduced pressure (150°C , $<1\text{mmHg}$) leaving a colourless viscous oil (14g) (1). A small quantity of higher molecular weight solid polyether was also obtained (ca 0.5g).

In addition dimethylpolyethylene glycol (500) has been modified by grafting with hexafluoropropene (ca 5.5 hexafluoropropyl units per molecule) and then perfluorinated in a similar manner to (3) yielding the perfluorinated polyether (1b).



Sample of (1) (labelled A2000) and of (1b) (labelled B500) (10.0g) have been dispatched to A. Davison, Euro. Off. Aerospace R+D (AFSC), 223/231 Old Marylebone Road, London NW1 5TH for forwarding to Wayne Ward at Wright Patterson AFB, Ohio. The sample container is marked F7LEOA 94W0447.

Characterisation of Intermediates/Products

Estimation of degree of hexafluoropropene incorporation

To an n.m.r. sample (CDCl_3 as solvent) was added 1 to 4 drops of α,α,α -trifluorotoluene. By determining the ratio of high field ^1H & ^{19}F n.m.r. integrals of the sample and trifluorotoluene it was possible to assess the extent of hexafluoropropene incorporation.

Estimation of degree of fluorination

To an n.m.r. sample (CDCl_3 as solvent in early stages of fluorination, neat in later stages) was added 1 to 4 drops of α,α,α -trifluorotoluene. By determining the ratio of high field ^1H & ^{19}F n.m.r. integrals of the sample and trifluorotoluene it was possible to assess the extent of fluorination knowing the extent of hexafluoropropene incorporation.

^{19}F N.M.R. of (1)

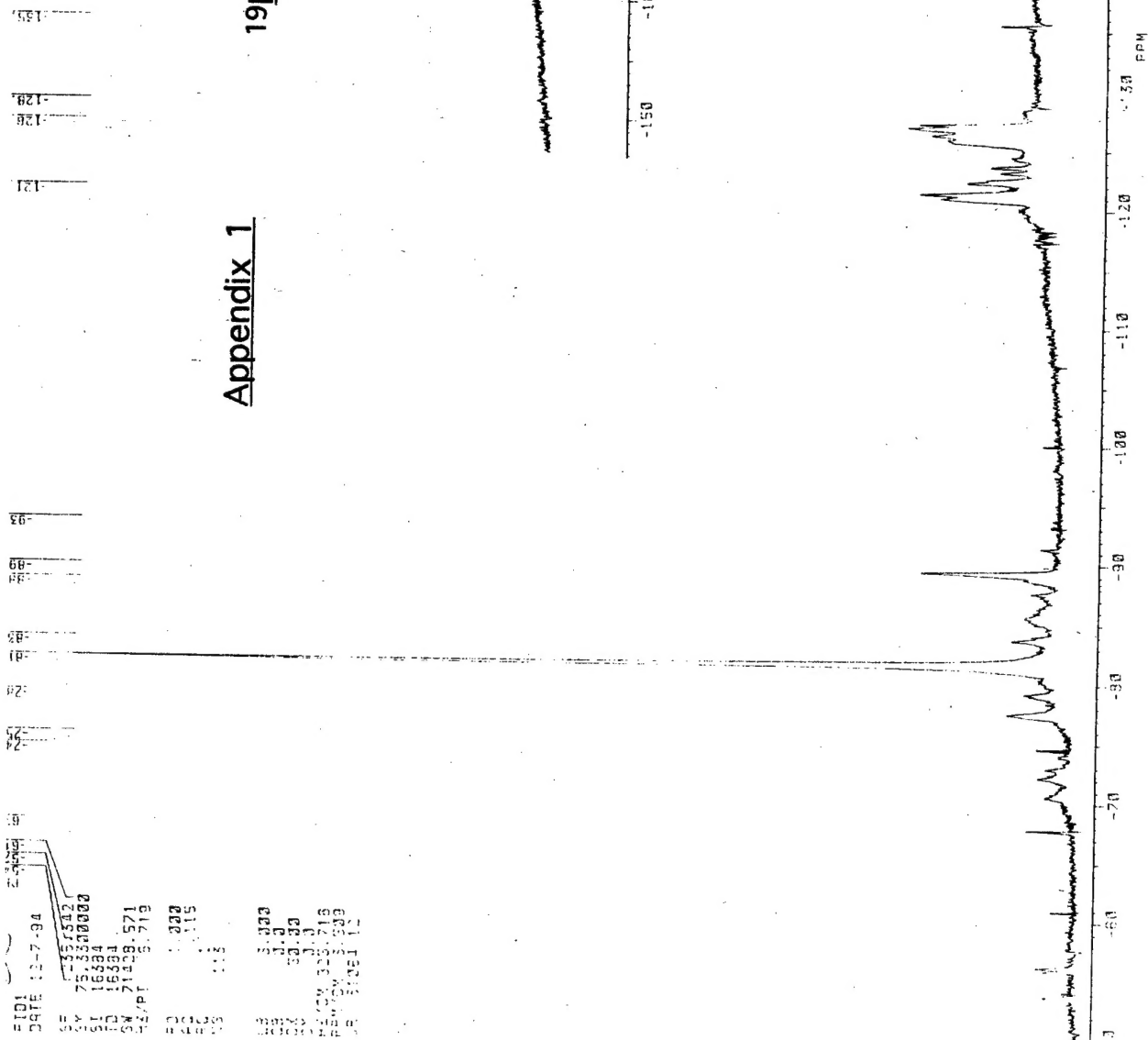
See Appendix 1 for 235MHz n.m.r. spectra of the samples

Summary

Perfluorinated polyethers of novel structure have been produced. Aspects of the larger scale synthesis of such materials have been developed.

Appendix 1

¹⁹F NMR spectrum of sample A2000



¹⁹F NMR spectrum of sample B500

